

Molecular Recognition via Hydroquinone–Quinone Pairing: Electrochemical and Singlet Emission Behavior of [5,10,15-Triphenyl-20-(2,5-dihydroxyphenyl)porphyrinato]zinc(II)–Quinone Complexes

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A popular methodology in the line of biomimetic chemistry for constructing porphyrin–quinones to study photoinduced electron transfer (PET) reactions involves the formation of noncovalently linked molecular systems. However, very few investigations have appeared in the literature,¹ mainly due to the associated synthetic difficulties. Ogoshi and co-workers^{1f–h} utilized two- and four-point H-bonding strategy, wherein the phenolic groups of the aromatic substituents on the porphyrin ring were used for the construction of noncovalently bound cofacial porphyrin–quinones. More recently, Sessler and co-workers^{1b–d} reported a sidewise-linked porphyrin–quinone system with a donor and acceptor separation of nearly 12 Å via base pairing. In this communication, we report yet another novel approach for forming noncovalently linked donor–acceptor complexes by pairing the “hydroquinone–quinone” entities, as shown in Chart 1.

The hydroquinone–quinone redox couple, which is involved in biological electron transport,² is also of special interest in the present study, since this strongly interacting pair would result in the formation of an altogether different redox couple, thus altering the energetics of the PET reaction originating from the photoexcited porphyrin. Moreover, in the present model, a small separation between the donor porphyrin and the acceptor hydroquinone–quinone has been achieved³ for this sidewise-linked system, thus facilitating a strong electronic coupling between them.

The hydroquinone-appended porphyrin, [5,10,15-triphenyl-20-(2,5-dihydroxyphenyl)porphyrinato]zinc(II) (**1**), was prepared according to the method of Rothmund and Mennotti⁴ by condensing pyrrole (4 mM), 2,5-dihydroxybenzaldehyde (1 mM), and benzaldehyde (3 mM) in propionic acid, followed by zinc(II) insertion.⁵ The compound **1** thus obtained was purified several times on basic alumina and by thin-layer chromatography.⁶ It is observed that addition of 10 equiv of easily reducible quinones, such as 2,6-dichloro-3,5-dicyano-1,4-benzoquinone (DDQ), to the solution of **1** results in a small blue shift of 2–3 nm for both the Soret and the visible bands

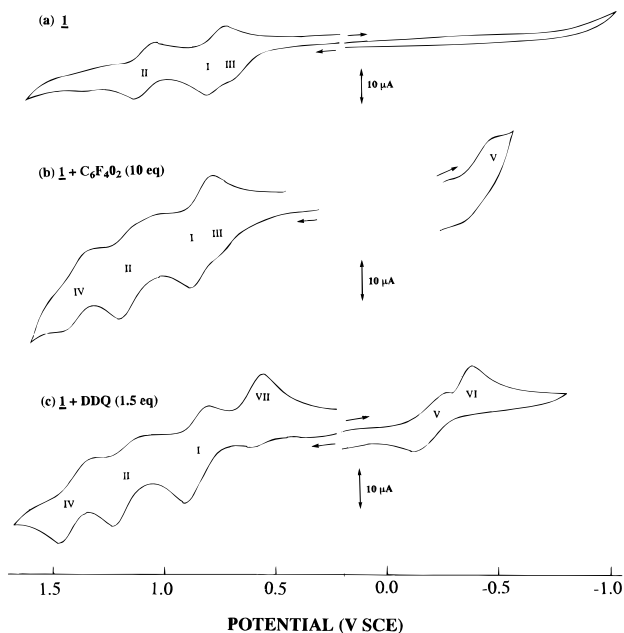
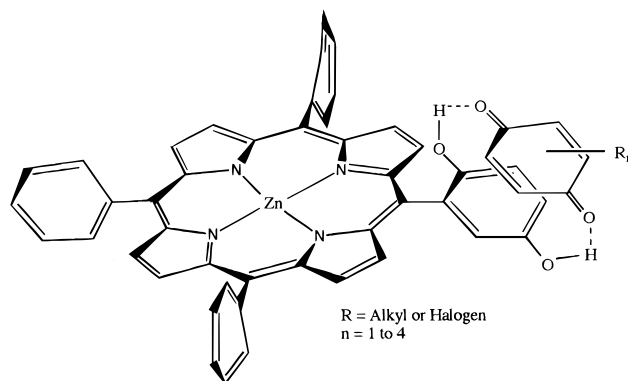


Figure 1. Cyclic voltammograms of (a) **1**, (b) **1** + tetrafluorobenzoquinone (10 equiv), and (c) **1** + DDQ (1.5 equiv) in benzonitrile containing 0.1 M TBAP. A strong one-electron reduction in the potential range 0.4 to –0.4 V is seen in (b), corresponding to the presence of 10 equiv of tetrafluorobenzoquinone in solution (see Table 1).

Chart 1



without any dramatic changes in the ϵ values, thus indicating the absence of π – π interactions.^{1f} The absence of π – π interactions is further confirmed by the ¹H NMR spectrum of **1** in the presence of 5 equiv of DDQ in CDCl₃.^{1f,7} The aromatic protons of the β -pyrrole and the triphenyl entities experience a downfield shift of <0.1 ppm, while the resonance corresponding to the OH protons of the hydroquinone entity are broadened in addition to experiencing a greater (~0.5 ppm) downfield shift, thus confirming the hydroquinone–quinone pairing.⁸

Electrochemical studies also provide evidence for the formation of a stable hydroquinone–quinone complex, and it is possible to evaluate its redox potentials within the molecule. Figure 1a shows the cyclic voltammogram⁹ of **1** in benzonitrile containing 0.1 M TBAP. The expected two ring-centered oxidations of porphyrins are easily detectable in **1**. These two oxidations are located at $E_{1/2} = 0.89$ and 1.21 V vs SCE (processes I and II), with a potential separation, $\Delta E_{1/2}$, of 310 mV. This $\Delta E_{1/2}$ agrees well with a 320 mV difference reported

(1) (a) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H. *J. Am. Chem. Soc.* **1990**, *112*, 9408. (b) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 345. (c) Harriman, A.; Magda, D. J.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 1530. (d) Harriman, A.; Kubo, Y.; Sessler, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 388. (e) Turro, C.; Chang, C. K.; Leroy, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 4013. (f) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1991**, *113*, 6233. (g) Hayashi, T.; Miyahara, T.; Hashizume, N.; Ogoshi, H. *J. Am. Chem. Soc.* **1993**, *115*, 2049. (h) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704.

(2) (a) Vervoort, J. *Curr. Opin. Struct. Biol.* **1991**, *1*, 889. (b) Walker, J. E. *Q. Rev. Biophys.* **1992**, *25*, 253.

(3) The center-to-center distance estimated from the CPK models for the complex in Chart 1 is about 6 Å, while the edge-to-edge distance is <1.5 Å.

(4) Rothmund, P.; Mennotti, A. R. *J. Am. Chem. Soc.* **1941**, *63*, 267.

(5) The free base porphyrin was converted to its zinc(II) complex by treatment with Zn(OAc)₂·H₂O.

(6) ¹H NMR in CDCl₃: δ 8.84 (m, 8H, pyrrole-H), 8.20 (m, 6H, meta-H of the triphenyl entity), 7.75 (m, 9H, ortho- and para-H of the triphenyl entity), 7–7.3 (m, 4H, substituted phenyl-H), 4.75 (s, 2H, phenolic-OH). UV–vis in PhCN: λ (nm) (log ϵ) 428 (5.81), 556 (4.32), and 598. The FAB mass spectrum revealed the molecular ion peak at $m/z = 709$ (calcd 709.4).

(7) (a) Fulton, G. P.; LaMar, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 2119; 2124. (b) Hill, H. A. O.; Sadler, P. J.; Williams, R. J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1663.

(8) The formation constant for hydroquinone–quinone is reported to be 0.083 mol^{–1} (see Eggers, B. R.; Chambers, J. Q. *J. Electrochem. Soc.* **1970**, *117*, 186).

Table 1. Reduction Potentials for the Quinone and Hydroquinone–Quinone Entities^a and the Optimum Concentration of Quinone Required To Saturate the Fluorescence Intensity of **1**^b

quinone	reduction potential ^c		[QQ'H ₂]/ [QQ'H ₂] ⁻	optimum concn (mM)
	Q/Q ⁻	Q ⁻ /Q ²⁻		
DDQ	0.56	0.25	-0.31 ^d	0.15
tetrafluorobenzoquinone	-0.03	-0.72	-0.49 ^d	0.86
tetrachlorobenzoquinone	-0.05	-0.73	-0.47 ^d	0.87
dichloronaphthaquinone	-0.47	-1.09	-0.82	1.20
1,4-benzoquinone	-0.55	-1.12	-1.26	1.21
methyl-1,4-benzoquinone	-0.56	-1.10	-1.33	1.30
naphthaquinone	-0.72	-1.20	<i>e</i>	3.03
2-methyl-1,4-naphthaquinone	-0.73	-1.16	<i>e</i>	3.44
duroquinone	-0.84	-1.42 ^c	<i>e</i>	4.08
2-methylanthraquinone	-0.92	-1.43	<i>e</i>	5.35
2-ethylanthraquinone	-0.97	-1.45	<i>e</i>	5.76

^a Formed by complexing the quinone with **1**. ^b The concentration of **1** employed for the fluorescence measurements was 20 μM. ^c In benzonitrile containing 0.1 M tetra-*n*-butylammonium perchloride. The potential values for quinone reductions agree with the literature values (see ref 12e). ^d E_{pc} at 0.1 V/s. ^e Reduction waves could not be isolated due to the overlap of porphyrin ring reductions.

for (*meso*-tetraphenylporphyrinato)zinc(II) [(TPP)Zn].¹⁰ A third oxidation process is also observed at $E_{pa} = 0.83$ V vs SCE (process III in Figure 1a), and this wave has been ascribed to the oxidation of the appended hydroquinone entity of **1**.¹¹

Addition of quinone to the solution of **1** decreases the current for oxidation corresponding to the hydroquinone, and a new oxidation process is observed in the potential range of 1.30–1.40 V, depending upon the type of quinone used for pairing. Figure 1b,c illustrates the cyclic voltammograms obtained in the presence of 10 equiv of tetrafluorobenzoquinone and 1.5 equiv of DDQ in a solution of **1** in benzonitrile. In the latter case, process III, corresponding to the oxidation of the hydroquinone, has completely vanished, and a new quasi-reversible wave, corresponding to the oxidation of the hydroquinone–quinone entity, is observed at $E_{1/2} = 1.40$ V vs SCE (process IV in Figure 1c).^{12,13} On complexing with quinone, the porphyrin ring oxidations (process I and II) experience a small anodic shift of 20 mV due to the electron-withdrawing nature of the neighboring hydroquinone–quinone. Similar observations have also been made with tetrafluorobenzoquinone, but in this case, a complete conversion using 10 equiv of quinone was not possible; however, the overall redox behavior remains the same. Changing the direction of the anodic scan shows additional waves (process VII) due to the secondary chemical reactions of the species produced at the electrode surface.^{10,12}

It has also been possible to obtain the reduction potential of the hydroquinone–quinone unit during the cathodic scan of the potential.^{12c,d} These processes are located at $E_{pa} = -0.49$ and -0.31 V vs SCE for tetrafluorobenzoquinone and DDQ complexes respectively (process V in Figure 1b,c). Table 1 lists

(9) Cyclic voltammograms were obtained with an IBM Model EC 225 voltammetric analyzer or on a EG&G Model 263A potentiostat using a three-electrode system. A platinum button or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The ferrocenium/ferrocene redox couple was used as the internal standard for potentials, and in 0.1 M TBAP–benzonitrile, its $E_{1/2}$ value was 0.45 V vs SCE.

(10) (a) Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435. (b) Davis, D. G. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Chapter 4.

(11) Hydroquinone in PhCN, 0.1 M TBAP, undergoes a two-electron irreversible oxidation at $E_{pa} = 1.08$ V vs SCE (see refs 12a–d).

(12) (a) Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 63. (b) Eggins, B. R. *Discuss. Faraday Soc.* **1974**, *56*, 276. (c) Parker, V. D. *Electrochim. Acta* **1973**, *18*, 519. (d) Eggins, B. R.; Chambers, J. Q. *J. Electrochem. Soc.* **1970**, *117*, 186. (e) Chambers, J. Q. In *The Chemistry of Quinonoid Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1974; Chapter 14.

(13) The DDQ–hydroquinone complex formed by treating an equimolar mixture of DDQ and hydroquinone undergoes oxidation at $E_{pa} = 1.48$ V vs SCE in benzonitrile containing 0.1 M TBAP.

the reduction potential for the hydroquinone–quinone entity formed by complexing the hydroquinone entity of **1** with different quinones, along with the reduction potentials of the free quinones. As expected, the observed reduction potentials for the hydroquinone–quinone entity are found to be dependent on the reduction potential of the free quinone used for pairing.

Dramatic changes in the fluorescence spectrum of **1** have been observed on addition of quinones. In benzonitrile, compound **1** fluoresces at 612 and 652 nm. Addition of DDQ (5 equiv) to a solution of **1** quenches the fluorescence intensity to over 90% of its original value; further addition leads to a point where the fluorescence intensity does not change significantly. Control experiments using (TPP)Zn show that addition of DDQ (10 equiv) decreases the fluorescence intensity by <3%. Further, a series of quinones which differ in their reduction potentials have also been employed, and Table 1 lists the optimum concentration of quinone required to saturate the fluorescence intensity. At the saturation point, the fluorescence intensity of **1** is around 10–15% and does not show any specific trend. An examination of Table 1 indicates that the concentration of the quinones required to reach the saturation is governed by the reduction potential of the hydroquinone–quinone entity, which in turn depends on the reduction potential of the quinone. This observation is suggestive of an electron transfer quenching mechanism, since it is known that the concentration of quencher needed depends on its reduction potential for an electron transfer mechanism.¹⁴ Alternatively, the different equilibrium processes involved may also be responsible for the observed behavior. However, as discussed below, the results on lifetime measurements indicate that the electron transfer process is the most likely quenching mechanism.

Lifetime measurements¹⁵ using single photon counting technique revealed that the photoexcited **1** decays monoexponentially, with a lifetime of 2.4 ns in deaerated benzonitrile. The quinone–hydroquinone complex formed by treating **1** with either DDQ or tetrafluorobenzoquinone just above their optimum concentrations needed to saturate the fluorescence intensity exhibited dramatic quenching of excited **1**. The decay of **1** bound to DDQ could be explained in terms of a three-exponential decay, with lifetimes of 0.10 (amplitude, 81%), 0.74 (0.16%), and 2.43 ns (3%), while a biexponential decay with lifetimes of 3.06 (24%) and 0.08 ns (76%) gave a satisfactory fit in the case of tetrafluorobenzoquinone-bound complex. The average lifetime of **1** complexed to DDQ is 0.25 ns, which is 89% smaller than the lifetime of the uncomplexed **1**. Similarly, the average lifetime of **1** is reduced by 67% on pairing it with tetrafluorobenzoquinone. A comparison of these results with the measured reduction potentials for the hydroquinone–quinone entity (Table 1) indicates that the efficiency of lifetime quenching depends on the reduction potentials (reduction of the hydroquinone–quinone entity in DDQ-derived complex is 180 mV easier than in the tetrafluorobenzoquinone-derived complex). These results are indicative of an electron transfer quenching mechanism. In general, the fluorescence lifetime of **1** on complexing with either DDQ or tetrafluorobenzoquinone is dramatically reduced, indicating an efficient dynamic quenching process in a porphyrin-bearing hydroquinone–quinone redox couple.

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(15) A mode-locked, synchronously-pumped, cavity-dumped Rhodamine 6G dye laser was used. The samples were excited at 578 nm, and the emission was monitored at 660 nm. Solutions containing **1** (50 μM) in the absence and presence of quinones in degassed benzonitrile were employed.